A Study of Concentration Fluctuations in the Binary Mixture Hexane-Nitrobenzene with X-ray Photon Correlation Spectroscopy

We have performed a small-angle x-ray scattering and x-ray photon correlation spectroscopy (XPCS) study of composition fluctuations in a critical binary mixture of hexane and nitrobenzene near its critical point. The measured critical exponents observed are consistent with expectations for this Ising system. The measurements demonstrate the feasibility of using XPCS to study the dynamics of even such a weak scatterer as this low-molecular-weight hydrocarbon fluid mixture.

X-ray photon correlation spectroscopy (XPCS) has the potential to measure the relaxation rate of the dynamic structure factor of materials over a wide range of time scales (1 µs to 1000 s) in and out of thermodynamic equilibrium at wave vectors inaccessible to visible light (0.004–2 Å^{-1}). XPCS experiments should expand our understanding of short length scale fluctuations, as well as enable studies of opaque materials, such as metal alloys. Most of the results reported to date have been performed on systems with a large length scale microstructure, which greatly enhances the scattered intensity because of the coherent addition of the scattering from the large number of atoms in the microstructure. Among the systems studied are aggregate systems such as colloids [1-4] and polymer micelles [5]; spinodally decomposing systems, such as sodium borosilicate glass [6]; and systems with antiphase domains, such as metal alloys [7,8]. Binary mixtures of low-molecular-weight fluids have much faster fluctuations (1 µs to s), and they typically scatter more weakly than systems studied previously.
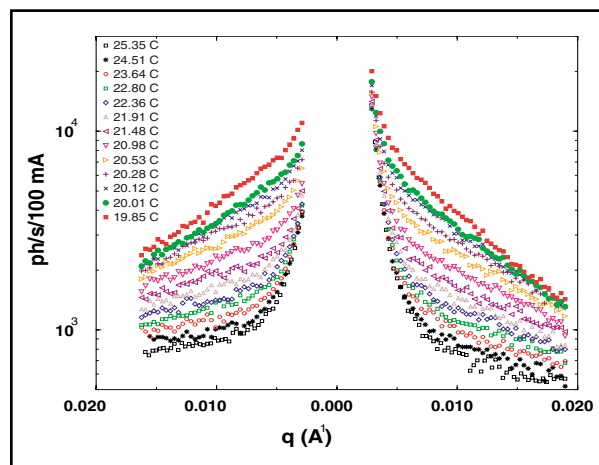

FIG. 1. Temperature dependence of SAXS from composition fluctuations, measured under incoherent conditions.

Here we report the first XPCS measurements done on a simple binary fluid, n-hexane (C_6H_{14}) and nitrobenzene ($C_6H_5NO_2$), near its critical point. We measured dynamic correlation functions with relaxation times as fast as 250 µs. Our measurements show that it is feasible to use XPCS to study the fast dynamics of even such weak scatterers as these low-molecular-weight hydrocarbon fluid mixtures. This work further demonstrates the general applicability of XPCS to a wide variety of materials.

This experiment was performed on the undulator beamline at sector 7 of the Advanced Photon Source, operated by MHATT-CAT. With the undulator fundamental set at 9.0 keV, the white beam was collimated with white beam slits to 100 µm x 100 µm. In the experimental hutch 36 m from the source, two small Pt-coated mirrors were used to produce a wide-bandwidth "pink beam." The doubly reflected beam had a bandpass of ΔE/E = 2.55% and an average energy of 8.7 keV. The coherent flux was 3.6 x 10^{10} ph/s

in a (8 μm)² beam incident on the sample. The speckle size in the detector plane was ~20 μm. The scattered x-rays in a single speckle were measured with an Amptek XR-100CR detector. A Brookhaven Instrument BI-30 hardware correlator was used to measure the dynamic correlation functions. The sample was mixed at the critical composition and placed in a sample cell consisting of a 3-mm-thick Al cylinder, sealed by two thin x-ray transparent Be windows. The sample temperature was stable to within 1 mK.

The mixture studied, n-hexane and nitrobenzene, has a relatively high x-ray contrast, making it a good choice for XPCS. Figure 1 shows the temperature dependence of the measured incoherent small-angle x-ray scattering (SAXS) scattering rate for the critical composition. The data clearly show the expected divergence in the susceptibility of the composition fluctuations as the critical temperature is approached. The data are well fit by Lorentzians with a critical temperature T_c = 19.12°C, a bare correlation length of 2.48 Å and critical exponents ν = 0.635 and γ = 1.23, in agreement with expectations for this Ising system.

When the scattering rate from composition fluctuations is measured under coherent conditions, the count rate ranges from 10 to 1000 ph/sec/speckle, depending on the scattering wave vector and the temperature. However, a more meaningful figure of merit for an XPCS experiment is the count rate per speckle per relaxation time. The relaxation times for composition fluctuations in the binary fluid mixture are given by the Stokes-Einstein relation:

$$\Gamma = 6\pi\eta\xi/(k_B Tq^2),$$

where η is the shear viscosity and ξ is the correlation length, which is temperature dependent. The shear viscosity of the mixture is 0.0053 P. The relaxation time of the fluctuations 0.1°C away from T_c for a wave vector of 0.002 Å⁻¹ is 244 μs, which can be sampled with a standard hardware correlator.

Figure 2 shows the dynamic correlation function of the scattered intensity versus the delay time of the correlator at ΔT = 0.063°C and q = 0.00156 Å⁻¹. The typical collection times to measure the correlation functions with the single-channel correlator
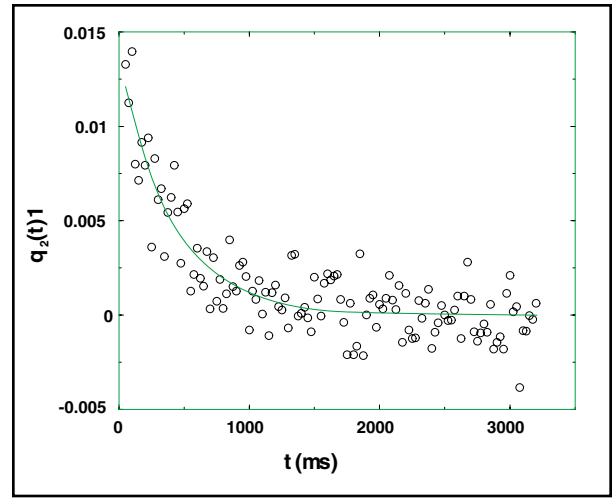

FIG. 2. Typical dynamic correlation function for scattering from composition fluctuations.

were on the order of 30 to 60 minutes. The typical contrast measured was about 1.4%. The measured relaxation times were quite reproducible. This consistency shows that the sample was not easily damaged by the x-ray radiation. In fact, none of our observations indicated that the sample was affected by the x-ray beam. This tolerance to high-intensity x-ray beam is remarkable among soft condensed matter, organic systems, such as colloids or polymers, which are generally much more susceptible to radiation-induced charging or damage effects. In this case, we speculate that the low viscosity of the mixture (comparable to the viscosity of water) and resulting high diffusion coefficient contribute to alleviating the effects of any radiation damage that may occur.
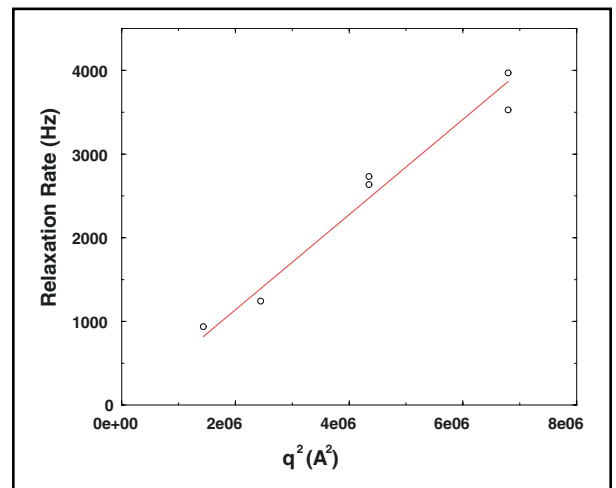

FIG. 3. Scaling of the relaxation rate with q^2.

Figure 3 shows the relaxation rate versus the square of the wave vector for the critical mixture at $\Delta T = 0.063°C$. The solid line is a fit to $\Gamma = Dq^2$ with a diffusion constant $D = 5.69 \times 10^8$ A^2/s. The data clearly show simple diffusive relaxation for the range of wave vectors shown. The measured diffusion constant is in good agreement with that expected from the Stokes-Einstein relation and the known viscosity of the mixture.

In summary, using a hardware correlator, we were able to measure the first XPCS dynamic correlation function on a simple binary fluid. Although they were rather fast (250 μs), we were able to measure the correlation functions with sufficient signal to noise within a single-channel correlator with an hour of collection time. The diffusion constant deduced from our XPCS measurement is consistent with the Stokes-Einstein equation, the known viscosity of the mixture, and the measured correlation length. We found no detectable signs of radiation damage in these mixtures even under the high intensity of a pink undulator beam at the APS.

Further developments in technique should permit future measurements to probe the relaxations on length scales much smaller than the correlation length, i.e., at large values of q^2. This is only possible in light scattering studies very near to the critical point, with very large correlation lengths. Studies of binary fluids in confined geometries should also benefit from this technique.

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